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PLASMA-SPRAYED POLY (METAL PHOSPHINATE) COATINGS FOR HIGH TEMPE--ETC(U)
JUL 77 J P KING, H D GILLMAN N62269-76-C-0507

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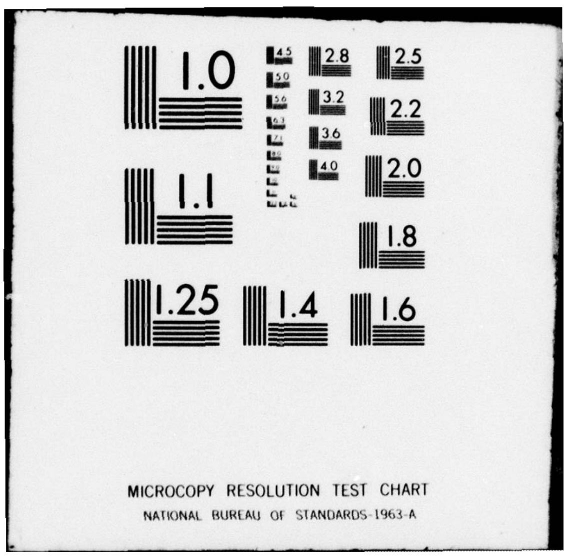
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6 PLASMA-SPRAYED POLY (METAL PHOSPHINATE) COATINGS FOR HIGH TEMPERATURE APPLICATIONS.

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22 September 1976 - 22 June 1977
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Warminster, Pennsylvania 18974

ABSTRACT

Pigmented and unpigmented diphenylphosphinates of chromium, zirconium, and zinc have been investigated as material for plasma-sprayed coatings. The aluminum-pigmented zirconyl diphenylphosphinate hydroxide system provided coatings having good adhesion, hardness, pigment-resin compatibility, and thermal stability. Infrared study of the coating materials before and after plasma-spraying indicated that the zinc and zirconium systems did not undergo any chemical change and that decomposition occurred in the chromium system.

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I. Background

Exploratory studies of poly(metal phosphinates) as potential coating materials were made at Pennwalt under a contract[1] with the Naval Air Development Center. Further investigation of poly-(metal phosphinates) as high temperature coating resins was sponsored at Pennwalt by the Air Force Material Laboratory.[2,3] The objective of this program was to develop thermally stable coatings (up to 1000°F) that could be cured at low temperature (below 300°F). This effort resulted in the development of solvent-based poly(metal phosphinate) coating formulations that could meet the target requirements. However, these coatings may not be the best possible based on poly(metal phosphinate) resins because the poly(metal phosphinates) used were not the most thermally stable. In fact, the coatings were thermally stable up to about 600°F, but at higher temperatures degradation of the organic portion of the coating material took place and the system became completely inorganic (mixture of metal oxides and phosphates). These residual coatings still retained the adhesion, optical, and hardness properties of the original system; however, the degradation process had caused the system to become porous and non-flexible. The more thermally stable poly-(metal phosphinates), i.e. those based on diphenylphosphinic acid, could not be used for these formulations because they were either infusible or insoluble or both. TGA study on these high temperature phosphinates in air showed that they were stable without any degradation up to about 1000°F.

An exploratory investigation was performed at Monsanto for the Air Force Material Laboratory during 1966-67[4] on new and improved polymeric coatings utilizing flame and/or plasma spraying as the coating deposition method. Plasma sprayed coatings of zinc diphenylphosphinate were among the best of those investigated in that program for thermal stability, hardness, and other properties.

The objective of this program has been to investigate the potential of more thermally stable poly(metal phosphinates) based on diphenylphosphinic acid as coating materials by plasma spraying. Particular emphasis has been placed on the poly(metal phosphinates) containing chromium, zirconium, and zinc centers.

II. Experimental

A. Preparation of Polymers and Their Blends

The hydroxybis(diphenylphosphinato)chromium polymer $\{Cr[OP(C_6H_5)_2O]_2OH\}_x$ was prepared by reaction of chromium trichloride hydrate with potassium diphenylphosphinate and potassium carbonate in a tetrahydrofuran-water mixture.[5,6] Attempts to grind this polymer in a ball mill with and without aluminum powder were unsuccessful because of agglomeration of the powders. Very fine (average particle size >100 μ) free-flowing powders were then obtained by grinding in a Waring blender. Pure $\{Cr[OP(C_6H_5)_2O]_2OH\}_x$ polymer and a 50% weight mixture of the polymer with 8 μ aluminum powder (1-131) from Reynolds Metal Co. were prepared.

The zinc bis(diphenylphosphinate) $\{Zn[OP(C_6H_5)_2O]_2\}_x$ was precipitated from an aqueous solution of zinc sulfate and potassium diphenylphosphinate.[7,8] It was also ground with a Waring blender (average particle size >100 μ). A 50% mixture with aluminum powder was similarly ground.

The zirconyl diphenylphosphinate hydroxide $\{ZrO(OH)-[OP(C_6H_5)_2O]\}$, which has not been reported in the literature, is a fine powdery white solid that does not melt even to 450°C. It was prepared by first neutralizing 0.5 mole of diphenylphosphinic acid with 0.5 mole of potassium carbonate in 700 ml of a 30% aqueous ethanolic solution and then adding it to 200 ml of H_2O containing 0.5 mole of zirconyl chloride. Even though an immediate precipitate was formed, the suspension was heated to 70°C for one hour and then let stand for an additional hour to insure complete precipitation. This polymer was then filtered off and dried at 125°C in air for 24 hours and then 110°C under vacuum for 8 hours. The solid was ground in a Waring blender to an average particle size of less than 100 μ. A 50% mixture with the aluminum powder was also ground with a Waring blender.

B. Pretreatment of Metal Surfaces

Panels of two alloys, titanium (Ti-6Al-4V) and aluminum (Fed. Spec. QQ-A-355), were selected as substrates for this investigation. Surface pretreatment of titanium panels has been previously reported.[2] Each panel was cut to the desired size (2" x 2" x 1/16"), scrubbed with an abrasive detergent such as Ajax (or sandblasted), and rinsed with distilled water. Each was then dipped in a copper sulfate solution, a mixture of acids ($HCl/H_3PO_4/HF$), and distilled water, respectively. Finally, the panel was rinsed with 2-propanol and acetone and allowed to dry in air. In the case of the aluminum alloy, the panels were cut to the desired size (2" x 2" x 1/16"), scrubbed with an abrasive detergent (Ajax). and rinsed with distilled water. They were then dipped in 2-propanol and acetone and allowed to dry in air.

C. Plasma-Spraying Equipment and Conditions

A 40 kw plasma-spraying gun and a standard high velocity electrode (Plasmadyne) were employed. Two levels of torch input power, 7.5 and 18 kw, were used in this study. Spraying distance between electrode and substrate ranged between 1.5 and 2.5 inches. Argon was employed as the arc gas with a flow rate ranging from

40 to 80 cfh, and helium was used as carrier gas with a flow rate varying from 12 to 75 cfh. Before a panel was sprayed, the distance between the substrate and electrode was first selected, and during the coating this distance was kept constant. The electrode was allowed to travel horizontally so that an area of approximately 2" x 3/4" was coated on each panel. In several cases, the electrode was maintained stationary, resulting in a coating area with a diameter of approximately one inch.

D. Evaluation of Coatings

The sprayed panels were evaluated for color, gloss, microscopic appearance, hardness, and adhesion. Evaluation of color and gloss was based on visual appearance. A binocular microscope was used to make observations on the coating integrity and pigment-resin compatibility. Pencil hardness determination was made on each panel. Adhesion rating was based on FTMS No. 141, Method 6301. Coating powders before and after plasma spraying were subjected to infrared analysis.

III. Results

A. Plasma-Sprayed Coatings of Zirconyl Diphenylphosphinate Hydroxide and Its Blend With Aluminum

Seven panels, two titanium and five aluminum, were coated with zirconyl diphenylphosphinate hydroxide. The coated panels were generally flat in gloss, light gray in color, and soft. Two of the specimens were coated by maintaining the electrode at a fixed position, resulting in slightly harder coatings. In general, titanium substrates provided slightly better coatings than those with aluminum substrates. There was no apparent fusion observed during spraying. Plasma spraying parameters and coating properties are summarized in Table I.

Seven panels, two aluminum and five titanium, were coated with aluminum-pigmented zirconyl diphenylphosphinate hydroxide. The coatings were flat in gloss, light gray in color, and had good adhesion. Some fusion was observed in most cases during spraying. The coatings, in general, were superior to those coated with the unpigmented resin. Additional properties and spraying parameters are recorded in Table II. Pigmented and unpigmented coating resins were subjected to infrared analysis before and after plasma-spraying. The IR spectra of these resins showed no change in band intensities or positions before and after plasma-spraying. Thus, no detectable thermal decomposition had taken place during plasma spraying of both unpigmented and aluminum-powder-pigmented zirconyl diphenylphosphinate hydroxide.

B. Plasma-Sprayed Coatings of Hydroxybis(diphenylphosphinato)-chromium and Its Aluminum-Pigmented Blend

Three aluminum and three titanium panels were coated with hydroxybis(diphenylphosphinato)chromium. The first specimen, which was coated by a slow-travelling electrode, showed poor adhesion. The remaining panels were coated by maintaining the electrodes at a fixed position. The coated specimens showed improved adhesion and slight fusion was observed in some cases. However, surface temperatures were quite high as indicated by intense discoloration on both sides of the coated panels. Other coating parameters and properties are listed in Table III.

Three aluminum and four titanium panels were coated with aluminum-pigmented hydroxybis(diphenylphosphinato)chromium. The coated specimens showed good properties such as hardness, adhesion, and resin-pigment compatibility. In most cases, fusion was observed during spraying. Additional properties and coating parameters are recorded in Table IV. The IR spectra of these plasma-sprayed chromium polymer samples showed a shift in the

P=O absorption from 8.9 μ to 8.65 μ and an increased intensity of the peak at 10.3 μ region when compared to the spectra of the original phosphinate material. This suggests that decomposition of both the unpigmented and pigmented chromium diphenylphosphinate took place during plasma spraying under the described conditions.

C. Plasma-Sprayed Coatings of Aluminum-Pigmented Zinc Bis(Diphenylphosphinate)

Several attempts to coat zinc bis(diphenylphosphinate) were unsuccessful because the fine powder was easily compacted and tended to obstruct the powder feeder, the tubing between the feeder and electrode, and the electrode itself. Three aluminum and two titanium panels were coated with aluminum-pigmented zinc bis(diphenylphosphinate). The properties of the coated specimens were comparable to those reported by Monsanto. Additional data are recorded in Table V. The IR spectra of a powder obtained by scraping from a coated panel were compared with an original sample of zinc bis(diphenylphosphinate). There was no indication of decomposition of the aluminum-pigmented zinc bis(diphenylphosphinate) during plasma spraying under the described conditions.

IV. Summary and Recommendations

Three poly(metal phosphinates), zirconium, chromium, and zinc bis(diphenylphosphinates), both unpigmented and pigmented with aluminum powder, were studied for their potential as plasma-sprayed coating materials. Two substrates, titanium and aluminum alloys, were employed for this investigation. The aluminum-pigmented resins in general provided better coatings than the corresponding unpigmented samples. Titanium substrates usually gave better adhesion than did the aluminum substrates. Some of the specimens coated with aluminum-pigmented zirconium and zinc polymers showed good adhesion, hardness, and resin-pigment compatibility. An infrared analysis of the coating materials before and after plasma-spraying of the unpigmented and aluminum-pigmented poly(metal phosphinates) was carried out. With the exception of the chromium system, no resin decomposition resulting from plasma-spraying under the described conditions was observed.

The aluminum-pigmented zirconyl diphenylphosphinate hydroxide appears to be the most promising system investigated so far in terms of overall coating properties and thermal stability. The zirconium diphenylphosphinate polymers having different atomic ratios of zirconium to phosphorus showed different softening ranges. A more detailed study of zirconium diphenylphosphinate polymers with different atomic ratios of zirconium to phosphorus is worthwhile. Emphasis in such an investigation should be placed on plasma-spraying parameters, reproducibility, and correlation between Zr/P ratios and overall coating properties.

V. References

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Table I. Zirconyl Diphenylphosphinate Hydroxide [$ZrO(OH)(OPPh_2O)$] Coatings

Specimen No.	4419-135-11-1	4419-135-12-1*	4419-135-13	4419-135-14	4419-135-15	4419-135-16	4419-135-17
Spray Process Variables							
Torch Input Power, kw	7.5	18	18	18	18	18	18
Spraying Distance, inch	2.0	2.0	2.0	2.0	1.5	1.5	1.5
Substrate Type	Al alloy	Al alloy	Al Alloy	Ti alloy	Al alloy	Al alloy	Ti alloy
He Carrier Gas, cfh	18	18	18	18	18	18	18
Ar Arc Gas, cfh	48	48	48	48	48	48	48
Other Remarks						Stationary Spray	Stationary Spray
Coating Properties							
Color	Lt. Gray	Lt. Gray	Lt. Gray	Gray	Lt. Gray	Lt. Gray	Gray
Thickness, mil	<0.5	0.5	1	1.5	2	2	1.5
Gloss	flat	flat	flat	flat	flat	flat	flat
Cracks	no	no	no	no	no	no	no
Pencil Hardness	3B	3B	5B	3B	6B	3H	9H
Tape Adhesion	fail (soft)	pass	pass	pass	pass	pass	pass
Appearance, 30X	Irreg. Surface	Fairly Smooth Surface	Fairly Smooth Surface	Fairly Smooth Surface	Fairly Smooth Surface	Fairly Smooth Surface	Portion fused; Good Smooth Surface

*Coated material was subjected to IR Analysis.

Table II. Aluminum-Pigmented Zirconyl Diphenylphosphinate Hydroxide Coatings

Specimen No.	4419-135-7	4419-135-8	4419-135-9	4419-135-23	4419-135-23A*	4419-135-24	4419-135-24A
<u>Spray Process Variables</u>							
Torch Input Power, kw	18	18	7.5	18	18	18	18
Spraying Distance, inch	2	2	2	2	2	1.5	1.5
Substrate Type	Ti alloy	Ti alloy	Ti alloy	Ti alloy	Al alloy	Ti alloy	Al alloy
He Carrier Gas, cfh	12	12	12	18	18	18	18
Ar Arc Gas, cfh	40	48	48	48	48	48	48
Other Remarks							
<u>Coating Properties</u>							
Color	Lt. Gray	Lt. Gray	Gray	Lt. Gray	Lt. Gray	Lt. Gray	Lt. Gray
Thickness, mil	10	2	1-2	5-8	5-8	1-2	2
Gloss	flat	flat	flat	flat	flat	flat	flat
Cracks	no	no	no	no	no	no	no
Pencil Hardness	8H	8H	>9H	>9H	>9H	>9H	>9H
Tape Adhesion	pass	pass	pass	pass	pass	pass	pass
Appearance, 30X	Fairly Smooth Surface; Good Resin-pigment compatibility	Fairly Smooth Surface; Good Resin-pigment compatibility	Fairly Smooth Surface; Good Resin-pigment compatibility	Irreg. Surface; Portion Fused	Irreg. Surface; Portion Fused	Fairly Smooth Surface; Good Resin-pigment compatibility	Smooth Surface; Portion Fused

*Coated material was subjected to IR Analysis.

Table III. Hydroxybis(diphenylphosphinato)chromium [$Cr(OPPh_2O)_2OH$] Coatings

Specimens	4419-135-18	4419-135-19	4419-135-20	4419-135-21	4419-135-21A*	4419-135-22
Spray Process Variables						
Torch Input Power, kw	18	18	18	18	18	18
Spraying Distance, inch	2.0	1.5	1.5	1.5	1.5	1.5
Substrate Type	Al alloy	Al alloy	Ti alloy	Ti alloy	Al alloy	Ti alloy
He Carrier Gas, cfh	18	18	18	18	18	18
Ar Arc Gas, cfh	48	48	48	48	48	48
Other Remarks		Stationary	Stationary	Stationary	Stationary	Stationary
Coating Properties						
Color	Greenish Gray	Greenish Gray	Gray	Lt. Brown	Greenish Brown	Dk. to Lt. Gray
Thickness, mil	<0.5	2-3	1.5	0.5	0.5	1.5
Gloss	flat	flat	flat	flat	flat	flat
Cracks	no	no	no	no	no	no
Pencil Hardness	4B (fairly soft)	9H	>9H	>9H	>9H	H-9H
Tape Adhesion	pass	pass	pass	pass	pass	pass
Appearance, 30X	Fairly Smooth Surface	Fairly Smooth; Portion Fused	Smooth Surface; Portion Fused	Smooth Surface; Portion Fused	Smooth Surface; Portion Fused	Irreg. Surface: Portion Fused

*Coated material was subjected to IR Analysis.

Table IV. Aluminum-Pigmented Hydroxybis(diphenylphosphinato)chromium [$Cr(OPPh_2O)_2OH$] Coatings

Specimen No.	4419-135-10	4419-135-11	4419-135-12	4419-135-25	4419-135-25A	4419-135-26	4419-135-26A*
Spray Process Variable							
Torch Input Power, kw	18	18	18	18	18	18	18
Spraying Distance, inch	2	2	2	2	2	1.5	1.5
Substrate Type	Ti alloy	Al alloy	Ti alloy	Ti alloy	Al alloy	Ti alloy	Al alloy
He Carrier Gas, cfh	15	15	15	18	18	18	18
Ar Arc Gas, cfh	48	48	48	48	48	48	48
Other Remarks							
Coating Properties							
Color	Lt. Gray	Lt. Gray	Lt. Gray	Gray	Lt. Gray	Gray	Lt. Gray
Thickness, mil	3	2	1-2	3-8	3-10	3-8	2-8
Gloss	flat	flat	flat	flat	flat	flat	flat
Cracks	no	no	no	no	no	no	no
Pencil Hardness	>9H	7H-9H	>9H	>9H	>9H	>9H	>9H
Tape Adhesion	pass	pass	pass	pass	pass	pass	pass
Appearance, 30X	Fairly Smooth Surface; Good Resin-Pig.Compat.: Small Portion Fused	Irreg. Surface; Good Resin-Pig.Compat.	Irreg. Surface; Good Resin-Pig.Compat.	Irreg. Surface; Portion Fused; Good Resin-Pig. Compat.	Irreg. Surface: Portion Fused; Good Resin-Pig. Compat.	Fairly Smooth Surface; Good Resin-Pig.Compat.	Irreg. Surface; Good Resin-Pig.Compat.

*Coated material was subjected to IR Analysis.

Table V. Aluminum-Pigmented Zinc Bis(Diphenylphosphinate) Coatings

Specimen No.	4419-135-1	4419-135-2	4419-135-3	4419-135-5*	4419-135-6
<u>Spray Process Variables</u>					
Torch Input Power, kw	18	18	18	7.5	18
Spraying Distance, inch	2	2.5	2.5	2.5	2.5
Substrate Type	Ti alloy	Al alloy	Al alloy	Al alloy	Ti alloy
He Carrier Gas, cfh	25	25	25	18	25
Ar Arc Gas, cfh	80	80	80	48	80
Other Remarks					
<u>Coating Properties</u>					
Color	Gray	Lt. Gray	Lt. Gray	Lt. Gray	Gray
Thickness, mil	7-10	6	10	5-10	4
Gloss	flat	flat	flat	flat	flat
Cracks	no	no	no	no	no
Pencil Hardness	3H-9H	HB	2H	HB	H
Tape Adhesion	pass	pass	pass	pass	pass
Appearance, 30X	Irreg. Surface; Portion Fused; Good Pigment-Resin Compat.	Irreg. Surface; Good Resin-Pig.Compat.	Irreg. Surface; Good Resin-Pig.Compat.	Irreg. Surface; Good Resin-Pig.Compat.	Irreg. Surface; Fair Resin-Pig.Compat.; White Spots

*Coated material was subjected to IR Analysis.